JAPANESE [JP,2001-007385,A]

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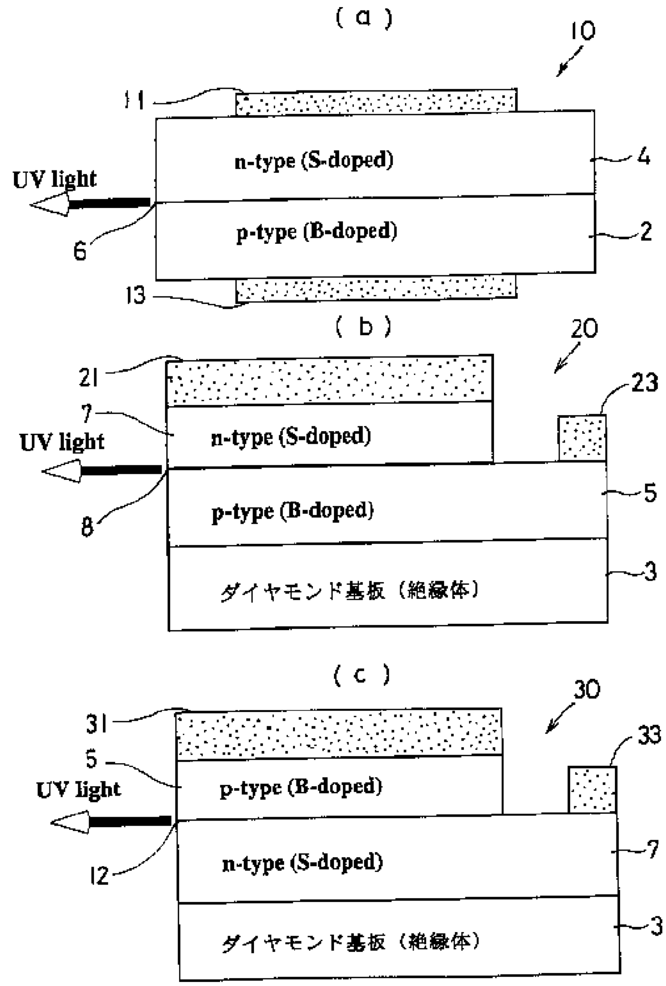
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention is used for luminescence of ultraviolet rays, the exposure of ultraviolet rays, elimination by ultraviolet rays, etc., and relates to an ultraviolet ray emitting device which emits light in ultraviolet rays, and a manufacturing method for the same especially by the pn junction of a diamond.
[0002]
[Description of the Prior Art]It is a very special semiconducting crystal with a band gap as large as 5.5 eV, and since this band gap is large and a diamond semiconductor has little change of the semiconductor characteristic by heat which is seen by the silicone device, the device manufacturing which operates at a remarkable elevated temperature is possible for it.
[0003]About the p type diamond semiconductor, the very

Drawing selection Representative draw



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quality diamond semiconductor thin film is obtained. The thing about 1500-$cm^2V^{-1}s^{-1}$ is obtained with sufficient reproducibility, and the hole mobility which is the typical characteristic has it. [enough for production of a high speed and a high current device]

[0004]Concerning [on the other hand,] a n type diamond semiconductor, it is difficult to obtain a n type good diamond semiconductor from the suitable donor atom not being found out conventionally, therefore the application had a limit, and the practical use device especially using pn junction was not able to carry out until production until it continued up to now.

[0005]Recently, composition of the n type diamond semiconductor used as the biggest solution technical problem about application of this diamond semiconductor was proposed by this invention persons (Japanese Patent Application No. No. 124682 [11 to]). In this proposal, the good n type diamond semiconductor is obtained by introductory ****** by making a sulfur atom into a donor during the diamond semiconductor crystal sulfur compounds and by adding hydrogen sulfide typically in the microwave plasma CVD. The electron mobility which is the typical characteristic is about 600-$cm^2V^{-1}s^{-1}$, and activation energy (impurity level) is about 0.38 eV. Although it is less than the thing of a p type diamond semiconductor at present, it is expectable that it is still adapted for a device fully.

[0006]

[Problem(s) to be Solved by the Invention]However, the diamond semiconductor device in which still good pn junction was formed does not have the semiconductor light device which was not obtained and used the pn junction of the diamond semiconductor, either. Although efforts to, manufacture a light emitting diode (it is hereafter described as "LED") and a semiconductor laser (it is hereafter described as "LD") over the wide wavelength range from ultraviolet to an infrared region on the other hand as a semiconductor light device are continued, there is still no semiconductor light device which emits light in ultraviolet rays.

[0007]Then, an object of this invention is to provide an ultraviolet ray emitting device with which ultraviolet rays can emit light from the pn junction of a semiconductor, and a manufacturing method for the same.

[0008]

[Means for Solving the Problem]To achieve the above objects, among this invention an ultraviolet ray emitting

device of the invention according to claim 1, It was a semiconducting crystal which has the bandgap energy corresponding to an ultraviolet region, and it had pn junction formed as a p-type semiconductor crystal which has an acceptor atom, and the n-type semiconductor crystal which has a donor atom, and ultraviolet rays were considered as composition which emits light by impressing forward voltage to pn junction. In addition to the above-mentioned composition, the invention according to claim 2 is characterized by a semiconducting crystal's being a diamond, a p-type semiconductor crystal's being a p type diamond semiconductor crystal, and an n-type semiconductor crystal being a n type diamond semiconductor crystal which doped sulfur as a donor atom. The invention according to claim 3 is characterized by a p-type semiconductor crystal being a p type diamond semiconductor crystal which doped boron as an acceptor atom.

[0009]In addition to the above-mentioned composition, the invention according to claim 4 is characterized by a p type diamond semiconductor crystal being the high voltage synthetic diamond which doped boron. The invention according to claim 5 is characterized by a p type diamond semiconductor crystal being a natural IIb diamond. The invention according to claim 6 has the structure which laminated a p type diamond semiconductor crystal and a p type diamond semiconductor crystal to an insulator diamond substrate. The invention according to claim 7 is characterized by donor atom concentration being the range of $10^{13}/cm^3$ - $10^{21}/cm^3$. The invention according to claim 8 is characterized by being the structure which pn junction joined by steepness of an atomic order.

[0010]By such composition, it has good and steep pn junction with an ultraviolet ray emitting device of this invention, and ultraviolet rays emit light by impression of forward voltage.

[0011]A diamond semiconductor device manufacturing method of the invention according to claim 9, The 1st process of forming a p type diamond semiconductor crystal layer in a vapor phase synthetic method with which a thin film grows based on activation of material gas, A donor atom is provided with the 2nd process of forming a n type diamond semiconductor crystal layer which is sulfur, and forms structure which carried out pn junction by steepness of an atomic order. In addition to the above-mentioned composition, in the 1st process, a dopant of a p type

diamond semiconductor crystal is boron, and the invention according to claim 10 is characterized by a ratio with carbon of hydrocarbon used as boron and sauce of a composition atom of a p type diamond semiconductor crystal being 20-20000 ppm. The invention according to claim 11 is characterized by a ratio with carbon of hydrocarbon used as sulfur and sauce of a composition atom of a diamond semiconductor crystal being 1000-10000 ppm in the 2nd process. The invention according to claim 12 is characterized by using at least one kind in electrical and electric equipment, heat, and light for activation of material gas in a vapor phase synthetic method.

[0012]By such composition, manufacture of an ultraviolet ray emitting device which has good and steep pn junction can be performed in a manufacturing method of an ultraviolet ray emitting device of this invention.

[0013]

[Embodiment of the Invention]Hereafter, the suitable embodiment by this invention is described based on drawing 1 - drawing 8. The band gap of a diamond is 5.5 eV (225 nm), and is the energy width of an ultraviolet region. As furthermore shown in drawing 1 and drawing 2, the cathode luminescence and photoluminescence of the n type diamond semiconductor which doped sulfur as a donor atom show having a light emission peak in 5.22 eV (237.7 nm). It turns out that it has the same light emission peak also in a good p type diamond semiconductor. Therefore, a diamond semiconductor is the optimal as an ultraviolet-rays luminescent material.

[0014]Drawing 3 (a) - (c) is an outline sectional view of the ultraviolet ray emitting device which emits light in ultraviolet rays using the pn junction of the diamond semiconductor concerning this invention. An arrow shows ultraviolet-rays luminescence from pn junction among a figure. When drawing 3 (a) is referred to, the ultraviolet ray emitting device 10 of this invention, On the p type diamond semiconductor crystal 2 formed from the high voltage synthetic diamond or the natural IIb diamond which doped boron, For example, with plasma CVD method, the n type diamond semiconductor crystal layer 4 which doped sulfur used as a donor atom is grown up, and the pn junction 6 is formed.

[0015]The diamond crystal called the IIb type which can produce the high voltage synthetic diamond which ************(ed), for example by 50kbar and a not less than 1500 ** ultra-high pressure elevated-temperature

method, and is produced naturally is a p type diamond semiconductor including boron.

[0016]The ultraviolet ray emitting device 20 shown in drawing 3 (b), The p type diamond semiconductor crystal layer 5 which was formed, for example with plasma CVD method on the insulator diamond substrate 3 formed from a usual synthetic diamond or natural diamond and which ************(ed), Besides the n type diamond semiconductor crystal layer 7 which carried out the sulfur dope with plasma CVD method is grown up, and the pn junction 8 is formed. The ultraviolet ray emitting device 30 shown in drawing 3 (c) makes reverse the conductivity type of the ultraviolet ray emitting device 20 shown in drawing 3 (b), and is formed.

[0017]The p type diamond semiconductor crystal layer 5 should just be about 1 nm or more, although thickness is about 1 micrometer. The doped boron concentration should just be more than $10^{13}cm^{-3}$, and a maximum is a $10^{21}cm^{-3}$ grade. In the p type diamond semiconductor crystal formed with the high voltage synthetic diamond or the natural IIb diamond which ************(ed), although thickness is about 500 micrometers, the thickness which can be formed may be sufficient. The boron concentration should just present a p type diamond semiconductor, and should just be more than $10^{13}cm^{-3}$.

[0018]The n type diamond semiconductor crystal layers 4 and 7 should just be about 1 nm or more, although thickness is about 1 micrometer. The sulfur concentration doped as a donor is more than $10^{13}cm^{-3}$, and a maximum is a $10^{21}cm^{-3}$ grade.

[0019]11, 13, 21, 23, 31, and 33 show an electrode among drawing 3 (a) - (c). These electrodes vapor-deposit titanium (Ti) on a diamond, for antioxidizing of the titanium, further, on it, vapor-deposit gold (Au) and use it as an electrode. The electrodes 23 and 33 of drawing 3 (b) and (c) may be formed in the rear-face side (exposure side) of an insulator diamond substrate.

[0020]Next, the characteristic of the ultraviolet ray emitting device of this invention is explained. Drawing 4 is a figure showing the analysis result of the depth direction of the impurity in the diamond semiconductor device shown by drawing 3 (b). By secondary ion mass spectrometry ("SIMS" is called hereafter.), analyze the ultraviolet ray emitting device 20 and the depth direction profile, The n type diamond semiconductor crystal layer 7 which carried

out the sulfur dope from the surface of the first pass, the p type diamond semiconductor crystal layer 5 which the secondary layer ************(ed), and the insulator diamond substrate 3 of the range shown by a figure Nakaya seal are shown in drawing 4. The profile shown by a and b is a background among drawing 4.

[0021]In the case of a diamond, as it has the feature that a heteroatom (B), for example, boron, sulfur (S), etc. hardly diffuse under the crystal, and this works in favor of formation of pn junction and shows drawing 4, change of the impurity concentration of an interface is very steep. That is, a p type diamond semiconductor crystal layer and a n type diamond semiconductor crystal layer change to an atomic order, and pn junction is formed. Therefore, the pn junction formed with the ultraviolet ray emitting device of this invention is dramatically steep to good quality and an atomic order.

[0022]Drawing 5 is a figure showing an emission spectrum when current is sent through a forward direction at the diamond semiconductor pn junction concerning this invention. Although the room temperature showed luminescence of the ultraviolet region strong against 237 nm (5.23 eV) and broadcloth luminescence has arisen also in the visible region simultaneously, the intensity is quite weaker than a 237-nm peak. Therefore, ultraviolet rays emit light from the pn junction interface of a diamond semiconductor.

[0023]The ultraviolet ray emitting device of this invention has a good rectifying characteristic into which current does not flow in the opposite direction, although current flows into a forward direction. Also in the elevated temperature of 400 ** and 500 **, it has a good rectifying characteristic.

[0024]Next, the manufacturing method of the ultraviolet ray emitting device of this invention is explained. The ultraviolet ray emitting device of this invention can be manufactured with a vapor phase synthetic method. As a vapor phase synthetic method, the electrical and electric equipment, heat, and the example by the microwave plasma CVD method of light energy which exploited electrical energy and thermal energy in this embodiment although what is necessary is just to have used either at least are shown according to the method of activating material gas. A sulfur dope n type diamond semiconductor is manufactured with the manufacturing method indicated to Japanese Patent Application No. No. 124682 [11 to] by this invention persons.

[0025]Drawing 6 is an outline lineblock diagram of the

microwave plasma CVD system used by this embodiment. As shown in drawing 6, the microwave plasma CVD system 40, For example, the 2.45-GHz microwave generator 41, and an isolator and the power monitor 43, The coil 47 which has the tuner 45 and with which microwave is irradiated, and the vacuum pump (not shown) which carries out evacuation of this coil 47, The gas supply line 49 which switches and supplies the mixed gas or the gas for a purge which is material gas to the coil 47, It has two or more optical windows 51 and 51, the substrate holder 53 provided in the coil, and the temperature control system 57 which heats or cools the insulator diamond substrate 55 installed on this substrate holder 53, gas is supplied on a substrate, and the microwave plasma 59 occurs. Substrate temperature is monitored with the optical pyrometer.

[0026]Next, an example of n type diamond semiconductor crystal growth conditions is shown in drawing 7. Reference of drawing 7 will use the mixed gas of volatile hydrocarbon / sulfur compounds / hydrogen, such as an alkane and an alkene, as material gas in this embodiment. Sulfur compounds are used as sauce of carbon whose hydrocarbon is a composing element of a diamond, and hydrogen as sauce of a donor atom is used as carrier gas.

[0027]As sulfur compounds, although organic sulfur compounds, such as inorganic sulfur compounds, such as hydrogen sulfide (H_2S) and carbon bisulfide (CS_2), and low-grade alkyl mercaptan, are mentioned, for example, hydrogen sulfide is the most preferred. Therefore, as mixed gas, it is preferred to use methane / hydrogen sulfide / hydrogen.

[0028]The concentration of volatile hydrocarbon in mixed gas is preferably good to use it at 0.5% - 3.0% 0.1% - 5%. The concentration of the sulfur compounds in mixed gas is preferably good to use [1 ppm - 2000 ppm] it at 5 ppm - 200 ppm.

[0029]In this embodiment, they are 1% of methane concentration, and 10-100 ppm of hydrogen sulfide. If the concentration of hydrogen sulfide increases, carrier concentration will increase, but in this range, 50 ppm of mobility are the most preferred from the place where the addition of hydrogen sulfide serves as the maximum at 50 ppm.

[0030]Although all the gas mass flows are based on the scale of a device, for example, the volume of a coil part, a distributed gas flow, displacement, etc., in this embodiment, they are 200 ml/min. Although a gas mass flow is controlled

by the massflow controller corresponding to each type of gas, for example using the mixed gas bomb of 100 ppm hydrogen sulfide / hydrogen, the addition of hydrogen sulfide is diluted with career hydrogen, and control of flow is carried out with a massflow controller, and it is controlled in proportion of a predetermined addition.
[0031]In this embodiment, the mixed gas bomb of 100 ppm hydrogen sulfide / hydrogen is used. Since hydrogen sulfide concentration is set as 50 ppm, when the full flow is 200 ml/min, if 100 ml/min is passed from the mixed gas bomb of 100 ppm hydrogen sulfide / hydrogen by making career hydrogen gas into 100 ml/min, hydrogen sulfide concentration can set it as 50 ppm on the whole.
[0032]In the microwave plasma CVD, atmospheric pressure is in about 30 to 60 Torr, and it was referred to as 40Torr in this embodiment. In microwave discharge, glow discharge is maintained by a comparatively high pressure. Although the temperature of the substrate which deposits makes a diamond 700 ** - 1100 **, in this embodiment, it is 830 **. Although a diamond semiconductor layer is grown homoepitaxially to the field (100) of an insulator diamond substrate, not only a field (100) but a field and a field (110) may be sufficient, for example (111).
[0033]Next, an example of p type diamond semiconductor crystal growth conditions is shown in drawing 8. It is preferred to use $CH_4/B_2H_6/H_2$ as mixed gas by this embodiment with reference to drawing 8. The diborane (B_2H_6) of a boron compound is used as sauce of an acceptor atom. As for CH_4 in mixed gas, 0.1-100 ppm and the B/C ratio of B_2H_6 are 20-20000 ppm 1.0%.
[0034]In this embodiment, the mixed gas bomb of 100 ppm diborane (B_2H_6) / hydrogen is used, and the diborane concentration introduced into a coil is set as 50 ppm. Although all the gas mass flows are 200 - 500 ml/min, in order to make the process of a n type diamond semiconductor follow, all the gas mass flows are made into 200 ml/min by this embodiment.
[0035]Although growing pressure is 40 - 50Torr, in order to make it follow the process of a n type diamond semiconductor, it is set as 40Torr of the same pressure. Although substrate temperature is 700 ** - 950 **, in order to make the process of a n type diamond semiconductor follow, it is 830 ** of the same temperature.
[0036]Next, the manufacturing method of the ultraviolet ray

emitting device of the structure shown in drawing 3 (b) is explained. First, the insulator (100) diamond substrate which carried out washing processing of the surface is installed in a substrate holder, After removing nitrogen and oxygen in several times repetition vacuum housing for a hydrogen purge from a gas supply line, while controlling heating a substrate holder so that substrate face temperature will be 830 **, pressure control is carried out to 40Torr. Substrate face temperature is measured with an optical pyrometer.

[0037]Next, while carrying out microwave discharge under the pressure control of 40Torr, If purge service-water matter gas and mixed gas are switched in a gas supply line and mixed gas 200 ml/min of methane 1%/diborane 50ppm / hydrogen is introduced into a coil, Plasma occurs in the substrate upper part, this plasma flow is supplied to an insulator diamond substrate, and a p type diamond semiconductor crystal layer grows epitaxially.

[0038]If it becomes predetermined thickness, a gas supply line will be switched, mixed gas 200 ml/min of 50 ppm of methane 1% / hydrogen sulfide / hydrogen is introduced into a coil, the generated plasma flow is supplied on the grown-up p type diamond semiconductor layer, and a n type diamond semiconductor layer grows epitaxially.

[0039]If it becomes predetermined thickness, while switching a gas supply line to a hydrogen purge, microwave discharge is suspended, and substrate heating is suspended or cooled. If it finally returns to a room temperature, from the substrate holder of the coil which carried out the ordinary pressure return, on an insulator diamond substrate, the ultraviolet ray emitting device which the p type diamond semiconductor crystal layer and the n type diamond semiconductor crystal layer laminated will be taken out, and an electrode will be vapor-deposited.

[0040]Thus, in the manufactured ultraviolet ray emitting device. Since pn junction is formed with the quality n type diamond semiconductor which doped the sulfur which serves as a quality p type diamond semiconductor and optimal donor, a good pn junction device is made, and if the forward current is sent, ultraviolet rays will emit light from a pn junction interface. Therefore, the very good ultraviolet ray emitting device with which ultraviolet rays emit light from a pn junction interface is producible.

[0041]

[Effect of the Invention]As explained above, in the ultraviolet ray emitting device of this invention, it has good

and steep pn junction, and has the effect that ultraviolet rays emit light from pn junction by impression of forward voltage. In the ultraviolet ray emitting device manufacturing method of this invention, it has the effect that manufacture of the ultraviolet ray emitting device which has good and steep pn junction can be performed.

[Translation done.]